

We claim:

1. A shaped article comprising:
 - a) polyvinylidene fluoride or copolymers thereof; and
 - b) a sufficient quantity of nucleating agent to initiate crystallization of the polyvinylidene fluoride or copolymers thereof at a significantly greater number of crystallization sites as compared to crystallization without the nucleating agent;wherein the shaped article is microporous and has been oriented in at least one direction at a stretch ratio of at least approximately 1.1 to 1.0
2. The shaped article of claim 1, wherein the sufficient quantity of nucleating agent is between approximately 0.2 percent to approximately 2.5 percent by weight of the polyvinylidene fluoride or copolymers thereof.
3. The shaped article of claim 2, wherein the nucleating agent is selected from the group consisting of Pigment Blue 60, Pigment Red 179, Pigment Violet 5:1, Vat Yellow 2, Pigment Yellow 24, and polytetrafluoroethylene.
4. The shaped article of claim 1, wherein the shaped article has been biaxially oriented.
5. The shaped article of claim 1 wherein the shaped article has micropores and the micropores are partially or completely filled with an additional substance.
6. The shaped article of claim 1, wherein the shaped article is in the shape of a tube, a sheet, a filament, or a hollow fiber.

7. The shaped article of claim 1, wherein the shaped article is coated with a coating material.
8. The shaped article of claim 1, wherein the shaped article is combined with at least one other material to form a laminated structure.
9. The shaped article of claim 1 wherein the polyvinylidene fluoride or copolymers thereof are semicrystalline and have a melt flow index between approximately 0.13 to approximately 6.0.
10. A shaped article comprising:
 - a) polyvinylidene fluoride or copolymers thereof;
 - b) a sufficient quantity of nucleating agent to initiate crystallization of the polyvinylidene fluoride or copolymers thereof at a significantly greater number of crystallization sites as compared to crystallization without the nucleating agent;
 - c) a diluent with which the polyvinylidene fluoride or copolymers thereof are miscible, and in which the polyvinylidene fluoride or copolymers thereof will dissolve at or above the melting temperature of the polyvinylidene fluoride or copolymers thereof, and will phase separate upon cooling to a temperature at or below the crystallization or phase separation temperature of the polyvinylidene fluoride or copolymers thereof;wherein the shaped article is microporous and has been oriented in at least one direction at a stretch ratio of at least approximately 1.1 to 1.0

11. The shaped article of claim 10, wherein the sufficient quantity of nucleating agent is between approximately 0.1 percent to approximately 1.0 percent by weight of the polyvinylidene fluoride or copolymers thereof and the diluent.

12. The shaped article of claim 11, wherein the nucleating agent is selected from the group consisting of Pigment Blue 60, Pigment Red 179, Pigment Violet 5:1, Vat Yellow 2, Pigment Yellow 24, and polytetrafluoroethylene.

13. The shaped article of claim 10, wherein the shaped article has micropores and the micropores are partially or completely filled with an additional substance.

14. The shaped article of claim 10, wherein the shaped article is in the shape of a tube, a sheet, a filament, or a hollow fiber.

15. The shaped article of claim 10, wherein the shaped article has been biaxially oriented.

16. The shaped article of claim 10, wherein the shaped article is coated with a coating material.

17. A method of making a microporous article, comprising the steps of:
a) melt blending to form a mixture comprising a polyvinylidene fluoride polymer or copolymers thereof, sufficient nucleating agent to initiate crystallization of the

polyvinylidene fluoride or copolymers thereof at a significantly greater number of crystallization sites as compared to crystallization without the nucleating agent, and glyceryl triacetate;

- b) forming a shaped article of the mixture;
- c) cooling the shaped article to a temperature at which the nucleating agent initiates the crystallization sites within the mixture so as to cause phase separation to occur between the glyceryl triacetate and the polyvinylidene fluoride or copolymers thereof; and
- d) stretching the shaped article in at least one direction at a stretch ratio of at least approximately 1.1 to 1.0

18. The method of claim 17, wherein the cooling comprises immersing the shaped article into a liquid cooling medium.

19. The method of claim 17, wherein the cooling comprises casting the shaped article onto a casting wheel.

20. The method of claim 17, wherein the orienting is biaxial orienting.

21. The method of claim 17, wherein the orienting provides a length increase in the article of from about 10 to about 1,000 percent of the original length of the article.

22. The method of claim 17 additionally comprising the step of removing the glyceryl triacetate.

23. The method of claim 22, wherein the glyceryl triacetate is solvent-soluble and the removing is by solvent extraction.
24. The method of claim 22, wherein the glyceryl triacetate is removed by volatilization of the glyceryl triacetate.
25. The method of claim 22 additionally comprising filling the microporous article with an additional substance.
26. The method of claim 25, wherein the additional substance is an ion conducting electrolyte.
27. The method of claim 25, wherein the ion conducting electrolyte is a proton conducting electrolyte.
28. The method of claim 17 additionally comprising the step of dimensionally stabilizing the article by heating the oriented article, while it is restrained, to a heat stabilizing temperature.
29. The method of claim 17 additionally comprising the step of laminating the microporous article to a second article.
30. The method of claim 17 additionally comprising filling the microporous article with an additional substance
31. The method of claim 29, wherein the additional substance is an ion conducting electrolyte.

32. The method of claim 31, wherein the ion conducting electrolyte is a proton conducting electrolyte.

33. An ion conductive membrane comprising:

a) a shaped article comprising:

polyvinylidene fluoride or copolymers thereof,

a sufficient quantity of nucleating agent to initiate crystallization of the polyvinylidene fluoride or copolymers thereof at a significantly greater number of crystallization sites as compared to crystallization without the nucleating agent, and

wherein the shaped article has been oriented in at least one direction at a stretch ratio of at least approximately 1.1 to 1.0 to provide a network of micropores wherein the micropore size is greater than approximately 0.4 microns, and the shaped article has a thickness less than approximately 1.5 mils and a Gurley less than approximately 10 sec/50cc; and

b) a sufficient quantity of ion conducting electrolyte filling the micropores to allow the membrane to function as a ion conductive membrane.

34. An ion conductive membrane of claim 33, wherein the sufficient quantity of nucleating agent is between approximately 0.2 percent to approximately 2.5 percent by weight of polyvinylidene fluoride or copolymers thereof.

35. An ion conductive membrane of claim 34 wherein the nucleating agent is selected from the group consisting of Pigment Blue 60, Pigment Red 179, Pigment Violet 5:1, Vat Yellow 2, Pigment Yellow 24, and polytetrafluoroethylene.
36. An ion conductive membrane of claim 33, wherein the polyvinylidene fluoride or copolymers thereof are semicrystalline and have melt flow indices between approximately 0.13 to approximately 6.0.
37. An ion conductive membrane of claim 33, wherein the shaped article is biaxially oriented at a stretch ratio of 1.1 to 1.0.
38. An ion conductive membrane of claim 33, wherein a sufficient quantity of ion conducting electrolyte is the volume of ion conducting electrolyte sufficient to fill at least approximately 95 to 100% or more of the pore volume of the membrane.
39. A membrane electrode assembly comprising the ion conductive membrane of claim 33.
40. An electrochemical device comprising the membrane electrode assembly of claim 39.
41. A fuel cell comprising the membrane electrode assembly of claim 39.
42. The shaped article of claim 1, said article comprising a membrane having an asymmetric structure.

43. The shaped article of claim 10, said article comprising a membrane having an asymmetric structure.